

US-PAT-NO: 4636327
DOCUMENT-IDENTIFIER: US 4636327 A
TITLE: Aqueous acid composition and method
of use
DATE-ISSUED: January 13, 1987

INVENTOR-INFORMATION:

NAME	CITY	STATE
Frenier; Wayne W.	Tulsa County	OK
N/A	N/A	
Wilson; David A.	Brazoria County	TX
N/A	N/A	

ASSIGNEE INFORMATION:

NAME	CITY	STATE
Dowell Schlumberger	Tulsa	OK
N/A	N/A	
Incorporated		

APPL-NO: 06/ 728448

DATE FILED: May 1, 1985

PARENT-CASE:

CROSS-REFERENCE TO RELATED APPLICATION

This is a continuation of application Ser. No. 526,723,
filed Aug. 26,
1983, now abandoned, which is a division of Ser. No.
213,280 filed Dec. 5,
1980, now U.S. Pat. No. 4,430,128.

INT-CL: [04] C23F011/14

US-CL-ISSUED: 252/87, 252/80 , 252/82 , 252/142 , 134/3
, 134/41

US-CL-CURRENT: 510/253, 134/3 , 134/41 , 510/264 ,

510/434 , 510/480

FIELD-OF-SEARCH: 252/80; 252/82 ; 252/87 ; 252/142 ; 134/3
; 134/41

REF-CITED:

PAT-NO		U.S. PATENT DOCUMENTS	
		ISSUE-DATE	PATENTEE-NAME
US-CL			
<u>3438901</u>		April 1969	Vassilef
	252/82	<u>N/A</u>	N/A
3527609		September 1970	<u>Vinso</u>
	134/3	N/A	N/A
<u>3664870</u>		May 1972	Oberhofer et al.
	134/3	<u>N/A</u>	N/A
3721629		March 1973	<u>Goodenough</u>
	134/3	N/A	N/A
<u>4250048</u>		February 1981	Leveskis
	134/3	<u>N/A</u>	N/A

FOREIGN-PAT-NO		FOREIGN PATENT DOCUMENTS	
US-CL		PUBN-DATE	COUNTRY
1577582		August 1969	FR
	252/82		
50-28063		September 1975	JP

ART-UNIT: 157

PRIMARY-EXAMINER: Wax; Robert A.

ATTY-AGENT-FIRM: White; L. Wayne

ABSTRACT:

Aqueous acid compositions are described which comprise (a) hydroxyethylethylenediaminetriacetic acid, and (b) a compatible acid corrosion inhibitor. The compositions are useful in removing iron oxide scale from metal surfaces.

9 Claims, 0 Drawing figures

Exemplary Claim Number: 1

BRIEF SUMMARY:

(1) BACKGROUND OF THE INVENTION

(2) 1. Field of the Invention

(3) This invention pertains to novel aqueous acid compositions comprising (a) hydroxyethylethylenediaminetriacetic acid (HEDTA), and (b) a compatible acid corrosion inhibitor. This invention also pertains to a method of using such compositions to chemically clean (remove) iron oxide scale from metal surfaces and a method of passivating the clean surface against corrosion.

(4) 2. Technology Review

(5) The invention utilizes an organic polycarboxylic acid referred to a hydroxyethylethylenediaminetriacetic acid (abbreviated as HEDTA). This known compound corresponds to the structural formula: ##STR1## HEDTA is a solid having a melting point of 159.degree. C. and it is soluble in both water and methanol. The ammonium and alkali metal salts of HEDTA are also known.

(6) HEDTA has been used in certain instances as a chelant. The ammoniated or aminated salts of HEDTA have also been used as chelants in removing scale from metal surfaces and for passivating ferrous metal surfaces. These salts were said to be effective against water hardness type scale (i.e. predominantly calcium and/or magnesium salts, such as calcium sulfate, calcium carbonate, etc.) and scales containing a high iron oxide content. See. U.S. Pat. No. 3,308,065 (Lesinski).

(7) A wide variety of other organic polycarboxylic acid

have also been used
in chemical cleaning and/or for passivating ferrous metal
surfaces. The
following printed publications are known to Applicant and
generally represent
the state of the art:

(1) _____ U.S. Pat. Nos.
3,072,502
3,595,799 3,308,065 3,627,687 3,413,160 3,639,279
3,438,811 3,668,009
3,438,901 3,684,720 3,492,238 3,806,459 3,510,351
3,510,432 3,547,697
Japanese Patents British Patents J5 0,022,721 1,518,321
J5 0,030,928
1,182,247 J5 3,125,937 J7 4,014,629 J7 8,044,895 USSR
Belgium 309,072
740,608 567,080 803,097 West Germany 2,054,067

(8) See also: NACE Corrosion '978, Atlanta, Ga. (1978):
Papers 38 and 208.

(9) In other instances, organic acids containing acid
groups other than
carboxylic acid groups have been presented as mimics of
polyalkylenepolycarboxylic acid chelants. See, for
example, U.S. Pat. No.
3,996,062 were polyalkylenepolyphosphonic acids (and alkali
metal or amine
salts thereof) are described. It is not known whether or
not such systems have
been commercialized.

(10) But, returning to the more relevant art, a review of
the above patents
shown that a variety of ammoniated or aminated
polyalkylenepolycarboxylic acids
have been described as useful chelants for chemical
cleaning. HEDTA is one of
the acids named. But this review also indicates that when
such compounds are
used, the pH is preferably weakly acidic or basic,
preferably basic. The use
of ammoniated ethylenediaminetetraacetic acid at pH of from
about 8.5 to about
10 (as per U.S. Pat. No. 3,308,065, U.S. Pat. No.
3,413,160 and/or U.S.

Pat. No. 3,438,811) continues to represent the state of the art from a commercial standpoint.

(11) To applicants knowledge, the prior art does not teach or suggest the invention now described.

(12) SUMMARY OF THE INVENTION

(13) A novel aqueous acid composition has now been discovered which is particularly useful in removing iron oxide scale from ferrous metal surfaces. The novel aqueous acid compositions have a pH of between about 1 and about 3 and comprise (a) hydroxyethylethylenediaminetriacetic acid (HEDTA), and (b) a compatible acid corrosion inhibitor.

(14) The novel compositions are particularly efficient in removing iron oxide scales from metal surfaces. HEDTA forms a chelate with dissolved iron and thus retains the iron in solution during chemical cleaning processes. While the novel compositions can be used in cleaning a variety of iron oxide-containing scales from metal surfaces, it is best suited for removing scales which are predominantly iron oxide. In addition, the "spent" aqueous acid composition can then be used to passivate the ferrous metal surface which is free or substantially free of iron oxide scale. This is accomplished by neutralizing the "spent" acid composition with an aqueous base (e.g. ammonium hydroxide) to a pH of from about 8 to about 10 and adding an oxidizing amount of (1) gaseous oxygen or gaseous air, and (2) an alkali metal nitrite to the composition.

(15) DETAILED DESCRIPTION OF THE INVENTION

(16) As noted above, the essential components of the novel aqueous acid compositions are well known. HEDTA can be prepared by any

of several known techniques, but it is preferably prepared by the process described by D. A. Wilson et al. in U.S. Pat. No. 4,212,994. The acid corrosion inhibitors are likewise a known class of compounds, any member of which can be used herein so long as it is compatible with aqueous solutions of HEDTA. I.e. the corrosion inhibitor is soluble in the aqueous solution and it does not substantially retard the efficiency of HEDTA in removing the scale and/or in chelating dissolved iron. The amine-based acid corrosion inhibitors are the most common and are thus preferred from a commercial availability standpoint.

(17) The novel acid compositions, as indicated, have a pH less than about 3. Preferably, the pH of the composition is from about 1 to about 2.

(18) Aqueous solutions of HEDTA usually have a pH of from about 2.2 to about 2.3. The pH of the novel acid compositions can be lowered by adding a compatible nonoxidizing inorganic acid. E.g. hydrochloric acid, sulfuric acid, phosphoric acid, and the like. Sulfuric acid is usually preferred when the composition is to be used in cleaning scale from a ferrous metal surface.

(19) The amounts of HEDTA in the novel acid compositions are bounded only by its solubility. Typically, HEDTA is present in amounts of from about 1 to about 8 weight percent, total weight basis. The amounts of corrosion inhibitor can likewise be varied. Functionally, the corrosion inhibitors will be present in sufficient quantities to inhibit or prevent acid corrosion of clean base metal (i.e. a corrosion inhibiting amount). Typically, the corrosion inhibitors are added in amounts of up to about 1 weight percent, total weight

basis.

(20) The novel aqueous acid compositions can be prepared by merely blending the essential components (i.e. water, HEDTA, and corrosion inhibitor). If an inorganic acid is to be included, it is normally added to an aqueous solution of HEDTA (with or without the corrosion inhibitor), according to standard procedures. Alternatively, the novel compositions can be prepared by generating the HEDTA in situ. In such an instance, an aqueous inorganic acid (such as 98 percent H₂SO₄) is blended into an aqueous solution of an ammonium or alkali metal salt of HEDTA (again, with or without the corrosion inhibitor present in the solution). It is preferable in such instances to either avoid the formation of a precipitate (e.g. Na₂SO₄) by having sufficient water present to dissolve the salts that are formed, or to remove the solid precipitates (e.g. by filtration). The reason for avoiding precipitates is readily apparent when the compositions are to be used in cleaning scale from metal surfaces having an unusual configuration, restriction zones or "valleys" that could be plugged by the solid.

(21) The process of cleaning (i.e. removing) predominantly iron oxide scale from metal surfaces involves contacting such scale encrusted surfaces with the novel aqueous acid compositions for a time sufficient to remove the desired amount of scale. Like most chemical reactions, the rate of scale dissolution is increased at higher temperatures. So while ambient temperatures can be used, the process is preferably conducted at an elevated temperature. The upper temperature is bounded only by the thermal stability of the essential components in the novel compositions and by the capacity or ability of the

corrosion inhibitor to function effectively at that temperature. Thus, process temperatures of up to about 200.degree. F. or more are operable, but temperatures of from about 160.degree. to about 180.degree. F. are normally preferred. The reaction rate of scale dissolution is quite acceptable at the preferred temperatures.

(22) After the cleaning process is complete, it is normally desirable to passivate the clean metal surface. This can be accomplished by draining the cleaning composition, rinsing the clean metal surface with water, and then contacting the clean metal surface with a passivating agent. Alternatively, and preferably in many instances, the "spent" aqueous acid compositions can be transformed into a passivating composition for ferrous metal by neutralizing them with an aqueous base (e.g. ammonium hydroxide, NaOH, etc.) to a pH of from about 8 to about 10 and adding an oxidizing amount of gaseous oxygen, gaseous air, and/or an alkali metal nitrite (e.g. sodium nitrite) to the neutralized composition. This can usually be done in situ without any need for the drain and rinse steps. Passivation is usually accomplished by contacting the clean ferrous metal while it is free or substantially free of iron oxide scale with the "spent" aqueous acid composition (as modified) at an elevated temperature. Temperatures of up to about 175.degree. F. are convenient and normally used; and temperatures of from about 150.degree. to about 160.degree. F. are generally preferred. The teachings of Teumac (U.S. Pat. No. 3,413,160) are applicable in this passivating step, and the disclosure by Teumac is incorporated herein by reference.

(23) The presence of an oxidant in the passivating compositions is

significant in enhancing the passivation process. The chelated iron in the "spent" aqueous acid composition is usually a mixture of chelated ferrous ($\text{Fe}^{\text{sup.}+2}$) and ferric ($\text{Fe}^{\text{sup.}+3}$) ions; a ratio determinable by Teumac's disclosure. Chelated ferric ion, of course, acts as an oxidant in the presence of base metal ($\text{Fe}^{\text{sup.}0}$), and so the "spent" aqueous acid composition can be neutralized (pH about 8-10) and used in passivation, by adding an oxidant to generate ferric ions. If the solution contains an anion that interferes with passivation (such as the sulfate anion), the "spent" solution must be neutralized (pH about 8 to 10) and oxidized with an oxidizing amount of (1) gaseous oxygen or gaseous air, and (2) an alkali metal nitrite. The passivation process can be monitored by measuring the electrical potentials of the metal surface in the passivating composition, as per Teumac. After passivation is complete, the passivating composition is used, drained and the passivated surface is flushed with water.

(24) In both the cleaning process step and the passivation step, it is advantageous to "circulate the system" so that fresh solution is continually brought to the metal surface.

DETAILED DESCRIPTION:

(1) EXPERIMENTS 1-3

(2) A three weight percent solution of HEDTA in water was prepared by dissolving the required amount of trisodium HEDTA salt in water and then lowering the pH of the solution to 1.6 using 98 percent sulfuric acid. Another solution of HEDTA was prepared by adding sulfuric acid to a three weight percent HEDTA solution in water to bring the pH to 1.2. A commercial

amine-based acid corrosion inhibitor (Dowell A175) was then added to each of the HEDTA solutions in amounts sufficient to give an inhibitor concentration of 0.3 weight percent. These aqueous acid HEDTA solutions, with inhibitor, were then evaluated as chemical cleaning solvents for iron oxide scale using the following procedure.

(3) A rusted water pipe having an original inside diameter of 0.5 inch was cut into uniform (6 inch) sections. A small closed test loop of stainless steel tubing (0.5 inch inside diameter) and one of the sections of rusted pipe was prepared and equipped with a liquid pumping means to circulate liquid through the closed loop. The test loop was then loaded with 400 mL of the chemical cleaning solution to be tested, the temperature of the contents raised to 100.degree. F., and the chemical cleaning solution pumped through the loop at a rate of approximately 200 mL/minute for 8 hours. The amount of dissolved iron in the cleaning solution was analyzed at the end of one hour and at the end of 8 hours using a commercial atomic absorption spectrophotometer. The results are summarized in Table I.

(1) TABLE I

Dissolved Iron (ppm)

Experiment	Solution	pH	1 Hour	8 Hours	Comments
90% clean	2 HEDTA				1 HEDTA 1.2 960 4240
1.6 1200 3840 90% clean remaining	3 EDTA*	5.0	360 1200		Much scale

*This solvent is an ammoniated ethylenediaminetetraacetic acid solution having a pH of 5 and is inhibited with a similar commercial aminebased corrosion inhibitor (Dowell A196).

(4) The data from Table I show the HEDTA solutions to be far more effective

in dissolving this predominantly iron oxide scale than the EDTA-based solution which is a commercial cleaning solvent.

(5) EXPERIMENTS 4-7

(6) In this series of experiments, the chemical cleaning ability of various solvents was measured by placing a one-inch "coupon" into a stirred autoclave containing 300 mL of the cleaning solution at 150.degree. F. for 6 hours. The amount of dissolved iron was measured at the end of one hour and at the end of the test, 6 hours. The one-inch "coupons" were cut from a piece of drum boiler tubing which had been used in a forced circulation boiler.

(7) The results from these tests are summarized in Table II.

(2) TABLE II

Dissolved Iron (ppm)

Experiment	Solution	pH	1 Hour	6 Hours	Comments
2560 Clean	5 HEDTA	1.6			4 HEDTA 1.2 2080
1760 2560 Clean	6 HEDTA	2.3	1280	2920	Some scale remaining
3440	7 EDTA*	5.0	1420		Some scale remaining

(8) In this series of experiments, the solvents used in Experiments 4 and 5 correspond to the solvents used in Experiment 1 and 2, respectively. A solvent used in Experiment 6 is a 3 percent aqueous solution of HEDTA containing 0.3 percent of corrosion inhibitor, Dowell A175. The EDTA solvent from Experiment 7 corresponds to the solvent used in Experiment 3.

(9) EXPERIMENTS 8-9

(10) This series of experiments is similar to those immediately preceding except that the "coupons" were sections of tubing from a pressure boiler referred to as a drumless boiler or a "once-through"

boiler. The types of scale are somewhat different. The results of the tests are shown on Table III.

(3) TABLE III

Dissolved Iron (ppm)						
Experiment	Solution	pH	1 Hr.	4 Hr.	6 Hr.	Comments
						8 HEDTA 1.6 3040
4200	-- clean/shiny	9				
EDTA 5.0	770 --	3220	clean			

(11) The solvents in Experiments 2 and 8 correspond and the solvents in Experiments 3 and 9 correspond. Experiments 8 and 9 were conducted at 150.degree. F. for 4 and 6 hours, respectively. The data show that the HEDTA solution was far more effective than the EDTA-based commercial solvent in removing the type of scale encountered in drumless boilers.

(12) EXPERIMENTS 10-12

(13) In this similar series of experiments, "coupons" obtained from a super heat/reheat section of a boiler were used. The data from this series of tests is summarized in Table IV.

(4) TABLE IV

Dissolved Experiment				
Solution	pH	T (.degree.F.)	Time (Hrs)	Iron (ppm)
				10 HEDTA 1.2 150 9
9152	11	HEDTA 1.6		
150	25	6136	12 EDTA* 5.0 200 25	7440

(14) The solvents used in Experiments 10-12 correspond to the solvents used in Experiments 1-3, respectively. In each instance, visual observation of the "coupon" and the spent cleaning solution showed the coupon to be clean with a small amount of Iron Chromite adhering to the surface. The data in Table IV show the HEDTA solutions to be as effective or better than the commercial

EDTA-based solvent even at lower temperatures against this heavy dense scale.
The scale on super heater/reheater surfaces is probably one of the most difficult scales to remove. The HEDTA results are, therefore, excellent.

(15) All of the dissolved iron figures presented in Tables I-IV were normalized to account for the difference in the weight of the "coupons".

(16) EXPERIMENTS 13-14

(17) An HEDTA solution was prepared (as per Experiment 2) at a pH of 1.6.
The pH of this solution was raised with ammonium hydroxide to a pH of 9.2. One percent sodium nitrite was then added, based on the weight of the original HEDTA solution. A steel specimen which had been freshly cleaned with acid was then placed into this passivating solution for fifteen minutes. The steel specimen was then removed, rinsed with deionized water and hung up to dry. No after-rusting was observed. Additionally, while the steel specimen was in the passivating solution, the surface potential of the steel coupon was measured against the standard Calomel electrode, as per the test set forth in Teumac. This potential also indicated passivation had occurred.

(18) In another passivation test, a steel coupon and a portion of a boiler tube which had been freshly cleaned with a HEDTA solution of pH 1.6 (as per Experiment 2) were rinsed and placed directly into hot water containing ammonia and 0.25 percent sodium nitrite for fifteen minutes. These metal articles were then removed, rinsed with deionized water, and hung up to dry. No after-rusting was observed. Similar results were achieved when the passivating solution contained 0.25 percent hydrazine instead of sodium nitrite.

(19) EXPERIMENT 15

(20) In a preoperational cleanup, one of two pipelines in a paper mill were cleaned by filling and circulating an aqueous solution containing 6 percent Na.sub.3 HEDTA and H.sub.2 SO.sub.4 at pH about 1.6 and from 0.3 weight percent of a commercial acid corrosion inhibitor (Dowell A175). The temperature of the solution was maintained between 140.degree. and 150.degree. F. After only 1.5 hours, the dissolved iron content had risen to and remained stable at 0.2 percent. The concentration of the Na.sub.3 HEDTA in the solution dropped to about 4 percent.

(21) A fresh solution of Na.sub.3 HEDTA/H.sub.2 SO.sub.4 of like strength and inhibitor concentration was prepared and circulated through the second system at a temperature of from 140.degree. to 150.degree. F. After 1.5 hours, the amount of dissolved iron in the solution was 0.3 percent and the concentration of the Na.sub.3 HEDTA had been reduced to about 3 percent and remained stable.

(22) The pH of the cleaning solution used on the first pipeline was 1.56 and the pH used in cleaning the second system was 1.97. Sulfuric acid was used in each instance to adjust the pH to the indicated values.

(23) Inspection of the cleaning system showed that the 0.01 inch thick deposit of dense magnetite had been completely removed from the pipeline. There remained, however, a gritty film on sections of the pipe. This grit was easily wiped off the pipe surface and was metallic in nature and could be picked up with a magnet. The customer was extremely pleased with the cleaning procedure. It was determined that the remaining material in the cleaning

system could be removed by a "steamblow" of the piping.

(24) It should be noted that the surfaces cleaned were composed of a myriad of metals, including T11 steel, 410 stainless steel, 4140 Cadmium-plated 304 stainless steel, T22 steel, Stillite surfaces and lead-plated steel rings. These metal surfaces were cleaned free or substantially free of the dense magnetite encrustations without any apparent adverse effect to the base metal. The results achieved in this field trial were excellent.

CLAIMS:

What is claimed:

1. An aqueous acid composition which can remove iron oxide scale from ferrous metal surfaces, the composition having a pH of between about 1 and about 3, and comprising (a) hydroxyethylethylenediaminetriacetic acid (HEDTA) dissolved therein in an amount of at least about 1% by weight of the composition, and (b) a compatible acid corrosion inhibitor.
2. The composition defined by claim 1 additionally comprising a non-oxidizing inorganic acid.
3. The composition defined by claim 2 wherein said inorganic acid is HCl or H.sub.2 SO.sub.4.
4. The composition defined by claim 3 wherein said inorganic acid is H.sub.2 SO.sub.4.
5. The composition defined by claim 1 wherein said HEDTA is generated in situ.
6. The composition defined by claim 4 wherein said HEDTA is generated in situ; said pH is from about 1 to about 2; and said acid

corrosion inhibitor
is an organic amine-based acid corrosion inhibitor.

7. The composition defined by claim 1 wherein said pH
is from about 1 to
about 2.

8. The composition defined by claim 4 wherein said pH
is from about 1 to
about 2.

9. A process for removing a predominantly iron oxide
scale from a ferrous
metal surface, said process comprising contacting said
scale with an aqueous
acid composition defined by claim 1.

US-PAT-NO:

4209418

DOCUMENT-IDENTIFIER: US 4209418 A

See image for Certificate of Correction

TITLE:

Gelatin benzimidazole blends as
inhibitors for
carboxylic acids

----- KWIC -----

Brief Summary Text - BSTX (4):

Acid cleaning operations are commonly employed to remove adhering substances, such as mill scale and fly ash, from the interior surface of vessels, tubes and related industrial processing equipment, particularly where such equipment is fabricated from ferrous metals. Aqueous processing equipment, especially that operating at elevated temperatures, tends to acquire a build-up of insoluble deposits. Typically, acid cleaning is used to remove these deposits. For example, acid cleaning is employed to remove lime deposits or water scale from power plant boilers and piping systems and evaporating equipment. Likewise, acid cleaning is employed to remove scale and deposits from processing equipment in such plants as refineries, utility companies, paper mills, chemical plants, and the like. Since cleaning acid tends to remove a portion of the basis metal of the industrial equipment with each cleaning, the use of inhibitors to minimize basis metal loss in acid cleaning can substantially extend the life of the equipment.

Brief Summary Text - BSTX (19):

(1) from about 75 to about 99.99 weight percent of an aqueous solution of at

least one carboxylic acid, the pH of said aqueous solution being between about 1.7 and about 7; and

Detailed Description Text - DETX (3):

The carboxylic acids employed in the cleaning solutions of the present invention may be present as an aqueous solution of one or more of the above-mentioned acids or as an aqueous solution of at least one ammoniated carboxylic acid. Suitable pH's for these aqueous solutions range from about 1.7 to about 7 (preferably from about 3 to about 6.5). The acid concentration in these aqueous solutions is not narrowly critical and can be any concentration as long as the aqueous solution pH is within the above-specified range. Preferably, the acid concentration in the aqueous solution is from about 1 to about 30 (more preferably from about 2 to about 20) weight percent based on the total amount of water and acid in said acid solution. The use of ammoniated carboxylic acids, particularly ammoniated citric acid, to remove copper-containing iron oxide scale from metal surfaces is known in the art, as disclosed in U.S. Pat. No. 3,072,502, incorporated herein by reference. The inhibitor blends of the instant invention have been found particularly effective in ammoniated EDTA and ammoniated citric acid/EDTA cleaning solutions.

Detailed Description Text - DETX (23):

Cleaning solutions were prepared by adding the inhibitor blend produced in accordance with Example 1 in an amount specified below, to 100 ml. of a 10 wt. percent aqueous solution of EDTA that had been ammoniated to a pH of 4.8 using NH.sub.4 OH (CP grade, 28-30 wt.-percent). As a comparison, cleaning solutions

were prepared using benzimidazole and gelatin as sole inhibitors in the amounts specified below.

Detailed Description Text - DETX (30):

Additional cleaning solutions were prepared by adding the inhibitor blends given in Table II to 100 ml. of an aqueous solution of 8 wt. percent EDTA and 4 wt. percent citric acid that had been ammoniated to a pH of 4.0 using NH.sub.4 OH (CP grade, 28-30 wt. percent). Inhibiting strength of the inhibitor blends was determined in accordance with the procedure given in Example 2 above.

Detailed Description Paragraph Table - DETL (1):

TABLE I

Amount of Inhibitor Run # Inhibitor of Ammoniated EDTA Cleaning Solution)	(grams in 100 ml (in grams)	Wt, Loss (lbs/sq ft/24	Wt, Loss (lbs/sq ft/24
hr)			
1.sup.(1) benzimidazole 5.0	0.3440	0.0156	2 gelatin 5.0
0.2061 0.0093 3			
gelatin 5.0 2-thio-4,6-dimethyl	0.1427	0.0065	pyrimidine
hydrochloride 0.1			
4 Gelatin 2.5 0.0599	0.0027	benzimidazole 2.5	5 gelatin
2.5 benzimidazole			
2.5 0.0599 0.0027 2-thio-4, 6-dimethyl		pyrimidine	
hydrochloride 0.1 6			
gelatin 1.7 benzimidazole 1.7	0.0414	0.0019	ethyl
quinolinium iodide 1.7			
7 gelatin 1.7 benzimidazole 1.7	0.0311	0.0014	ethyl
quinolinium iodide 1.7			
2-thio-4, 6-dimethyl pyrimidine hydrochloride		0.1	

.sup.(1) Run 1 was made using a cleaning solution have a pH of 4.5. All other runs were made at a pH of 4.8.

Claims Text - CLTX (10):

(1) from about 75 to about 99.99 weight percent of an aqueous solution of at least one carboxylic acid, the pH of said aqueous solution being between about 1.7 and about 7; and

Claims Text - CLTX (17):

(1) from about 75 to about 99.99 weight percent of an aqueous solution of at least one ammoniated carboxylic acid, the pH of said aqueous solution being between about 3 and about 6.5; and

Current US Cross Reference Classification - CCXR (1):
134/3

Current US Cross Reference Classification - CCXR (2):
134/41

US-PAT-NO: 4587043

DOCUMENT-IDENTIFIER: US 4587043 A

TITLE: Decontamination of metal surfaces in
nuclear power reactors

----- KWIC -----

Abstract Text - ABTX (1):

A method for decontaminating metal surfaces having radioactive oxide deposits thereon is disclosed which comprises preparing a decontamination solution having a pH of about 1.5 to about 4 comprising water, about 0.02 to about 0.5% of a water soluble organic acid which has an equilibrium constant in a complex with ferric ion of at least about $10^{9.9}$ and which is capable of producing a pH of about 2 to about 3 in water, and about 0.01 to about 0.4% of a chelate in free acid form which has an equilibrium constant in a complex with ferric ion of about $10^{15.15}$ to about $10^{19.19}$ and which is at least 0.4% soluble at 40.degree. C. in water having a pH of about 2 to about 3. An apparatus for performing the above method is disclosed.

Brief Summary Text - BSTX (7):

These deposits can form on the inside surfaces (primary surfaces) of the primary loop of a pressurized water reactor, or in the steam generator core, or in the piping inbetween. The deposits could also form on the steam generating side (secondary surfaces) of the steam generator, but there the problem is much less severe because the radioactivity is lower and the deposits are more easily dissolved. In a boiling water reactor the deposits can

form on turbine blades or in any part of the cooling loop. In a high temperature gas reactor, the deposits can form on the primary cooling loop. Generally, the deposits formed in pressurized water reactors are the most difficult to remove, so if a process and composition can remove those deposits, it can also remove deposits formed in other types of reactors.

Detailed Description Text - DETX (11):

The decontamination solution used in the process of this invention solubilizes metal ions and removes radionuclides by forming a complex with them. The decontamination solution comprises water, about 0.02 to about 0.5% of an organic acid, and about 0.01 to about 0.4% of a chelate. (All percentages herein are by weight and are based on solution weight.) Preferably, the decontamination solution comprises about 0.05 to about 0.3% of the organic acid and about 0.03 to about 0.2% of the chelate, the rest being water. We have found that if less organic acid is used the DF falls off and if more of the organic acid is used the apparatus being cleaned may corrode. Also, it increases the quantity of ion exchange resin waste and may reduce the cation exchangeability. If less chelate is used, a precipitate may form which does not dissolve readily, and if more chelate is used there will be a larger residual metal concentration in the solution due to less ion exchangeability. Both effects decrease the DF. The total decontamination solution should have a pH between about 1.5 and about 4 and preferably between about 2 and about 3. (The organic acid must only be capable of producing a pH of about 2 to about 3, but slightly higher and lower pH's are obtained in the presence of the chelate at higher temperatures.) The temperature of the

decontamination solution should
be about 70.degree. to about 200.degree. C.

Detailed Description Text - DETX (12):

The acid in the decontamination solution must be organic because inorganic acids can leave residual ions which can cause corrosion problems in the reactor. Organic acids, on the other hand, decompose to produce only water and carbon dioxide. The organic acid must have an equilibrium constant for complexing with the ferric ion of at least 10^{10} because the metal ions may precipitate if the equilibrium constant is less than about 10^{10} . The organic acid must be capable of giving a pH of about 2 to about 3 in water because a lower pH can cause corrosion and chelate precipitation, and a higher pH reduces the DF. Suitable organic acids include citric acid, tartaric acid, oxalic acid, picolinic acid, and gluconic acid. Citric acid is preferred because it is inexpensive, non-toxic, readily available, and has reasonable radiation stability.

Detailed Description Text - DETX (13):

The chelate must have an equilibrium constant for complexing with the ferric ion between about 10^{15} and about 10^{19} . If the equilibrium constant of the chelate is less than 10^{15} the metal ions may precipitate and a lower DF obtained. If it is greater than about 10^{19} the metal ions may not leave the complex with the chelate and attach to the ion exchange resin. The chelate preferably should be soluble in water having a pH of about 2 to about 3 at at least 0.4%. Also, the chelate must be in the free acid form, not the salt form, because the cation which forms the salt would be removed on the ion exchange column and then the resulting acid form can

precipitate, thus plugging the column. Suitable chelates include nitrilotriacetic acid (NTA), and hydroxyethylenediaminetriacetic acid (HEDTA). NTA is preferred as it gives a higher DF, it is more soluble, it leaves less residual iron and nickel in the apparatus being decontaminated, it has the lowest solution activity levels of cobalt 60, and it can chelate more metal per unit of chelate. Ethylenediaminetetracetic acid (EDTA) has not been found to be suitable in the process of this invention, as it is not readily ion exchangeable. This means that metal ions cannot be removed from the EDTA complex efficiently in an ion exchange column. The result is that residual cobalt is left in solution with the EDTA. While this can be removed with anion exchange resins, that results in a loss of the EDTA reagent. Also, EDTA has a lower solubility than NTA, so more dilute solutions and higher temperatures must be used. As a result, the process takes longer and requires higher pressures which increase handling and operational difficulties.

Detailed Description Paragraph Table - DETL (1):

Cumulative DF	After 1st Decon	After 2nd Decon	After Decontamination	Solution pH
Oxidation				
30/30/40% mixture of citric/oxalic/NTA	1.5	1.04	1.09	31.3
1. Solution dissolved (@ 50.degree. C.) slowly at about 50.degree. C.				
30/30/40% mixture of citric/oxalic/NTA	1.5	1.00	1.01	25.1
2. Greater than 50% (@ 50.degree. C.) clean metal on coupon ID's.				
30/30/40% mixture of citric/oxalic/HEDTA	1.65	1.08	1.08	19.4
1. Solution dissolved (@ 25.degree. C.) rapidly at 25.degree. C.				
30/30/40% mixture of citric/oxalic/HEDTA				

1.65 1.05 1.05 18.5 2.
Clean metal plus (@ 25.degree. C.) oxide on coupon ID's.
30/30/40% mixture of
citric/oxalic/EDTA 1.9 1.04 1.20 52.2 1. Solution
dissolved (@ 60.degree.
C.) slowly at about 50.degree. C. 30/30/40% mixture of
citric/oxalic/EDTA
1.9 1.07 1.07 48.4 2. Mainly clean metal (@ 60.degree.
C.) on coupon ID's and
spent solution precipitated on cooling.

Claims Text - CLTX (4):

(2) about 0.02 to about 0.5% of at least one
water-soluble organic acid
which has an equilibrium constant in a complex with ferric
ion of at least
10.sup.9, and which is capable of producing a pH of 2 to 3
in water; and

Claims Text - CLTX (5):

(3) about 0.01 to about 0.4% of a chelate in free acid
form which has an
equilibrium constant in a complex with ferric ion of about
10.sup.15 to about
10.sup.19, and which is soluble at at least 0.4% at
40.degree. C. in water
having a pH of about 2 to about 3;

Current US Cross Reference Classification - CCXR (3):

134/3

US-PAT-NO: 6423152

DOCUMENT-IDENTIFIER: US 6423152 B1

TITLE: Method and apparatus for treatment
of internal surfaces in a closed-loop fluid system

----- KWIC -----

Brief Summary Text - BSTX (5):

Below various types of scale are described where chemicals and solvents frequently are utilised for scale removal: Algae growth and other organic deposits, e.g. in pipe networks supplying water for consumption, fire-fighting facilities and process water. Pipe networks can have major dimensions, e.g. in water mains from reservoirs to cities, and smaller dimensions such as in buildings and ships. Percipitation deposits of cabonates, phosphates or other chemical compounds that over time may precipitate from a fluid flow. Sedimentation deposits of organic compounds such as oil, kerosene, fat and vax deposits in pipelines. Corroton deposits arising with oxidation over time, such as on inner surfaces in pipe systems and tanks.

Current US Cross Reference Classification - CCXR (4):
134/22.12